Japanese Kokai Patent Application No. Hei 1[1989]-146974

Translated from Japanese by the Ralph McElroy Company, Custom Division
P.O. Box 4828, Austin, TX 78765 USA

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JAPANESE PATENT OFFICE

PATENT JOURNAL

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INK-JET RECORDING LIQUID

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[There are no amendments to this patent.]

Claims

1. An ink-jet recording liquid, characterized by the fact that it contains a water-soluble dye and β-cyclodextrin.

2. An ink-jet recording liquid noted in Claim 1, in which the dye concentration is 0.01-1.0 wt%.

3. An ink-jet recording liquid noted in Claim 1, characterized by the fact that it is a recording liquid for recording the same color using not less than two inks with different dye concentrations and is the lighter ink among the above.

4. An ink-jet recording liquid noted in Claim 1, in which the concentration of the β-cyclodextrin is 1-2 mol per 1 mol of the dye.

Detailed explanation of the invention

Industrial application field

Said invention relates to a recording liquid (hereafter referred to as ink) used in ink-jet recording. More specifically, it relates to an ink that provides an image with a superior light resistance even in the light-colored part or mixed-color part in a variable density ink method.

Prior art

The ink-jet recording method is attracting attention as one form of nonimpact technology in which full colorization is easy. In particular, it is suited for printers with regard to factors

such as the texture, color reproduction, tone variety, etc., as a recording method in a printer, such as a personal computer graphic (CG) that prints hard copies and a video printer that prints out video images.

Various methods have been proposed as the ink-jet recording method; we have already proposed an ink-jet recording method (variable-density ink method) using not less than two inks having different dye densities with regard to not less than one among yellow, magenta, cyan, and black inks.

According to said method, an ink for highlighting (light ink) and an ink for darkness (dark ink) are used so that smooth color reproduction is possible with a wide density range from the highlighted part to the dark part of the image.

Problems to be solved by the invention

However, in said variable-density ink method, there was a great merit in using a light ink in the image formation, but there was a problem in the light resistance of the formed image. Namely, there was a problem of the light resistance being less in the image part using the light ink than in the image part using dark ink.

Generally, in ink-jet recording, a water-based ink is often used as the ink, namely, a water-soluble dye is used as the recording agent, thus although the tone of the image is superior, there was a problem in the lightfastness of the image, thus selecting the dye was difficult. In particular, when using the dark ink at a density of a given degree, the fastness of the image was insufficient due to the generation of fading when used

in the low-density area as a light ink even when it has a relatively high degree of fastness.

Said problem of light resistance intrinsic to a light ink is considered to originate in the aggregated state of the dye molecules. Namely, dye molecules in the high-density state form large aggregates due to many molecules aggregating in the ink; even when this is recorded on recording paper, relatively large molecular aggregates are maintained, thus a superior light resistance is manifested. However, when the dye density is low, namely, in the case of a light ink, even if the molecular aggregate is formed, the size is small, with a few molecules, thus a sufficient aggregated state cannot be achieved even on the recording paper, it has a tendency to receive impact by the radical type or active oxygen (singlet oxygen), etc., generated by light, and the light resistance is low.

Therefore, the objective of said invention is to provide an ink-jet ink in which image formation with a superior light resistance is possible even if it is a light ink with a low dye density.

Also, another objective of said invention is to provide an ink-jet ink that forms an image with a superior light resistance in the light-colored part and dark-colored part using the variable-density ink method.

Means for solving the problems

Said objectives are achieved with said invention as noted below.

Namely, said invention involves an ink-jet ink characterized by the fact that it contains a water-soluble dye and β-cylcodextrin.

Function

By including β-cyclodextrin in an ink, in particular, a light ink with a relatively low dye density, the dye molecules are enclosed in the β-cyclodextrin; even after being recorded on recording paper, the assault by the harmful radicals or singlet oxygen generated by light is minimized and the light resistance of the image is improved.

The exact mechanism for the β-cyclodextrin added to the ink in improving the light resistance of the dye in the ink is not known, but it is considered to be due to the following.

Namely, when the dye exists in the ink at a density that can form (self-association) an aggregate, namely, in the case of a dark ink, the coloring part of each dye molecule is protected by the three-dimensional obstacle provided by the adjacent molecules during the aggregation and makes assault (energy mobility and electron mobility) by the harmful radicals (·OOH, ·CO) and singlet oxygen generated by ultraviolet rays and visible light difficult.

On the other hand, when the dye molecules cannot form an aggregate or even when possible the aggregates are composed of a few molecules, namely, in the case of a light ink, protection of coloring part by self-association cannot be expected. Therefore, the supposition is that the coloring part is protected by the dye

being enclosed by a compound such as β-cyclodextrin and the lightfastness of the image is improved.

Favorable applied modes

Next, said invention will be explained in detail with favorable applied modes.

The ink of said invention is composed of, for example, water, water-soluble dye, water-soluble organic solvent, wetting agent, and other additives; said components and blending proportions can be similar to the conventional publicly known ink-jet recording inks and are not restricted in particular.

The ink of said invention is obtained by blending β-cyclodextrin simultaneously when preparing an ink from said components. As the quantity of β-cyclodextrin added to the ink, about 1-2 mol per 1 mol of dye is the most favorable range with respect to the dye in the ink. When it is less than this range, the effect of improving the light resistance is insufficient; when it is greater, problems such as precipitation of the ink, an excessive increase in the viscosity of the ink, etc., are created, so this is not favorable.

Said invention is particularly effective in light ink. A light ink as referred to in said invention refers to that with a dye density of about 0.01-1 weight [sic; g/L], although it differs according to the modulation of the tone-expression capacity, for example, the dot diameter of the used ink-jet recording head (Gould's method using a piezo element), the change in the dot-driving count or driving pattern (dithering pattern) per picture element with a fixed dot diameter (bubble jet method,

cyclonix [transliteration] method), or the recording paper used. Furthermore, it is of course possible for the dye density to be changed by the size of the molecular absorption coefficient of the dye. Namely, light ink refers to an ink that reproduces at a reflection density of 0-0.5, preferably 0-0.3, in the highlighted part during the image composition.

Said invention is effective as a light ink when forming a color image by preparing an ink colored yellow (Y), magenta (M), or cyan (C)--and according to necessity, when using a black (Bk) ink--and using not less than two variable-density inks in which at least one related to the same color differ(s) in density.

In this case, the discoloration in the mixed-color part and fading of the light-colored part occurred quickly in the conventional method and lacked light resistance of the color image as a whole, but in said invention said light-colored part and mixed-color part, in particular the part containing a magenta dye, has a superior light resistance so a color image with superior light resistance is provided in the image as a whole.

With regards to the dye, one can effectively use water-soluble dyes such as an acidic dye, direct dye, etc., applied in the conventional ink, but it is particularly effective to use dyes that fade easily in the light-colored part, for example, magenta dyes of C.I. acid red 35, 37, etc.

Application examples

Next, said invention will be explained in further detail by citing application examples.

Application Example 1

Table I

	Ink A	Ink B	Ink C
C.I. acid red 35	2.0 parts	1.0 part	0.5 part
Distilled water	49.0 parts	50.0 parts	50.2 parts
Diethylene glycol	30.0 parts	30.0 parts	30.0 parts
Polyethylene glycol	10.0 parts	10.0 parts	10.0 parts
N-methyl-2-pyrrolidone	9.0 parts	9.0 parts	9.0 parts
B-cyclodextrin			0.3 part

After composing according to the recipe noted in said Table I and stirring the composition for 1 h, magenta light inks A and B and magenta light ink C of said invention were obtained by filtering with a cotton blend filter of 0.5 μm.

Comparative Example 1

Magenta light ink D of the comparative example was prepared, which excluded the β-cyclodextrin in the blend of ink C among the inks in Application Example 1.

Application Example 2

Magenta light inks E and F and magenta light ink G of said invention were obtained by blending in the same manner as Application Example 1 by substituting C.I. acid red 35 with C.I. acid red 37.

Comparative Example 2

Magenta light ink H of the comparative example was obtained, which excluded the β-cyclodextrin in the blend for ink G among the inks in Application Example 2.

The following tests were executed with regards to the inks in Application Examples 1 and 2 and Comparative Examples 1 and 2, then the performance was compared.

(1) Light resistance (monochrome)

Using the Ink-jet Color Printer RP-601 (Canon, Inc.), color patches were created in a size of 2 cm x 2 cm, total irradiation for 10 h was executed with a Canon Fade-Ometer Ci-35F (product of Atlas Electric Co.), and the color difference ΔE* (color difference of L*a*b color space) before and after the irradiation was computed. The evaluation with ΔE* = 0-3 was noted as ○, ΔE* = 3-7 as Δ, and ΔE* = 7-15 as X.

(2) Evaluation of light resistance of the image

Similarly using an RF-601 printer, a human image that included the face of a female was recorded, changing only three colors of the magenta shade out of the 8 colors of said printer with the inks of the application examples and comparative examples. The evaluations were made such that for a case in which the fading in the skin color part hardly changed after 100 h of irradiation at Ci-35F, the result was given as ○, when the change was slightly noticeable it was Δ, and when the change was

significant, it was x. The results are shown in Table II below.

Table II

	Monochrome	Image
Ink A	o	o
Ink B	o	o
Ink C	o	o
Ink D	x	x
Ink E	o	o
Ink F	o	o
Ink G	o	o
Ink H	x	x

As is apparent from Table II above, whereas the light resistance of the image composed of the light ink with a low dye density and containing a suitable amount of β-cyclodextrin was superior, the ink that does not contain β-cyclodextrin faded noticeably and the image quality was degraded.

Effects

As noted above, by adding β-cyclodextrin, the light resistance of the image composed of said ink is improved. In particular, using the light ink containing β-cylcodextrin among the inks used in the ink-jet recording method provided with a dark ink and light ink in correspondence in order to express the highlighted part and dark part of the image, the light resistance in the monochrome [samples] and light resistance with mixed colors in the image improved.

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1. An ink-jet recording liquid, characterized by the fact that it contains a water-soluble dye and β-cyclodextrin.

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3. An ink-jet recording liquid noted in Claim 1, characterized by the fact that it is a recording liquid for recording the same color using not less than two inks with different dye concentrations and is the lighter ink among the above.

4. An ink-jet recording liquid noted in Claim 1, in which the concentration of the β-cyclodextrin is 1-2 mol per 1 mol of the dye.

Detailed explanation of the invention

Industrial application field

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Prior art

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Various methods have been proposed as the ink-jet recording method; we have already proposed an ink-jet recording method (variable-density ink method) using not less than two inks having different dye densities with regard to not less than one among yellow, magenta, cyan, and black inks.

According to said method, an ink for highlighting (light ink) and an ink for darkness (dark ink) are used so that smooth color reproduction is possible with a wide density range from the highlighted part to the dark part of the image.

Problems to be solved by the invention

However, in said variable-density ink method, there was a great merit in using a light ink in the image formation, but there was a problem in the light resistance of the formed image. Namely, there was a problem of the light resistance being less in the image part using the light ink than in the image part using dark ink.

Generally, in ink-jet recording, a water-based ink is often used as the ink, namely, a water-soluble dye is used as the recording agent, thus although the tone of the image is superior, there was a problem in the lightfastness of the image, thus selecting the dye was difficult. In particular, when using the dark ink at a density of a given degree, the fastness of the image was insufficient due to the generation of fading when used

in the low-density area as a light ink even when it has a relatively high degree of fastness.

Said problem of light resistance intrinsic to a light ink is considered to originate in the aggregated state of the dye molecules. Namely, dye molecules in the high-density state form large aggregates due to many molecules aggregating in the ink; even when this is recorded on recording paper, relatively large molecular aggregates are maintained, thus a superior light resistance is manifested. However, when the dye density is low, namely, in the case of a light ink, even if the molecular aggregate is formed, the size is small, with a few molecules, thus a sufficient aggregated state cannot be achieved even on the recording paper, it has a tendency to receive impact by the radical type or active oxygen (singlet oxygen), etc., generated by light, and the light resistance is low.

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Means for solving the problems

Said objectives are achieved with said invention as noted below.

Namely, said invention involves an ink-jet ink characterized by the fact that it contains a water-soluble dye and β-cylcodextrin.

Function

By including β-cyclodextrin in an ink, in particular, a light ink with a relatively low dye density, the dye molecules are enclosed in the β-cyclodextrin; even after being recorded on recording paper, the assault by the harmful radicals or singlet oxygen generated by light is minimized and the light resistance of the image is improved.

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